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Mechanical properties of thermally cycled nylon bonded Nd-Fe-B permanent magnets

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The effect of thermal cycling on the stress-strain behavior of polyamide (nylon) and polyphenylene-sulfide (PPS) based injection molded Nd-Fe-B magnets was investigated after test specimens were cycled between −40 and 150°C for 50, 500, or 5000 repetitions. It was found that PPS based magnets exhibit higher ultimate strengths, higher modulus and lower toughness than nylon based magnets. Furthermore, formulations containing platelet morphology particles exhibited higher strengths and modulus than those containing spherical morphology particles, with increases in particle volume fraction leading to a decrease in strength. Differences in strength, modulus, and toughness were attributed to the degree of bonding between the matrix and the magnet powder in the various formulations, the degree of crosslinking, along with the effects of powder morphology. Additionally, it was found that while the stiffness of these materials increased with thermal cycling, their toughness decreased significantly, by as much as 99%. The extent of these effects was found to be dependent on the polymer matrix, powder morphology, and volume fraction of powder in the magnet. Finally, it was found that the PPS composites showed less relative change due to thermal cycling than the Nylon composites.

1. Introduction

Injection molding has been demonstrated as a cost-effective high-volume method for the near net-shape production of isotropic bonded $Nd_2Fe_{14}B$-based magnets. In this process, polyamide (nylon) or polyphenylene-sulfide (PPS) are commonly used as the polymer binder forming the matrix for the intermetallic magnetic powder in the injection molding system. These plastics are favorable for use in this application due to their good corrosion resistance, high dimensional stability, and light weight.

Additionally, two types of Nd-Fe-B particles may be utilized in the composite system. Traditional melt-spun powder will possess an irregular platelet morphology, which will tend to align their long axes with the direction of material flow during injection molding. These powders will have an average thickness of $\approx 30\ \mu$m and an average size of 10–400 μm. Powders produced by gas atomization on the other hand tend to have a spherical morphology and range from 5 to 90 μm in size with an average size of $\approx 50\ \mu$m.

Work has been done to compare the effects of polymer binder system and powder morphology on the mechanical characteristics of injection molded Nd-Fe-B-based bonded magnets at various operation temperature ranges. Although the mechanical properties of these magnet systems have been evaluated over a range of temperatures, the effects of thermal cycling on these properties has not been evaluated. Thermal cycling will be important to consider if these magnets are used in applications such as automobile engine components where service temperatures may range from below zero to upwards of 180°C. In this paper, we report the effects of thermal cycling on the mechanical properties of bonded Nd-Fe-B magnet specimens exposed to 50, 500, or 5000 thermal cycles between −40 and 150°C. Mechanical characterization was then carried out and results were compared to those obtained previously for as-produced bonded Nd-Fe-B magnetic materials.

2. Background

Despite their well-characterized magnetic properties, only limited mechanical testing has been performed on Nd-Fe-B permanent magnets. The bulk of this testing has been performed on the more mature technology of sintered magnets containing alloying elements such as transition metals or lanthanide elements [1–4] as opposed to the bonded magnets discussed in this work. Such work has reported fracture toughness (K_{IC}) values ranging from 1.2–5.5 MP$\sqrt{a}$, bending strength values ranging from 130–300 MPa, compressive strength values ranging from 750–1060 MPa, and tensile strength values ranging from 50–140 MPa. The range in these values has been found to be largely due to the amount (and type) of alloying element addition, rare earth constituents and the oxygen content in the materials, and the overall magnet composition. To the knowledge of the authors, no mechanical testing or analysis has been performed on thermally cycled rare earth-based permanent magnets.

Mechanical testing results have been reported on as-produced injection molded bonded Nd-Fe-B permanent magnets [5, 6]. The magnets tested possessed both the nylon and PPS binder systems and utilized both the platelet and spherical particle morphologies. Tensile testing was conducted at fixed temperatures ranging from −40 to 180°C, while flexural testing was only performed at 23°C.

The ultimate tensile strength of plain nylon containing no filler (magnetic powder) was shown to be higher than or equivalent to both those of formulations consisting of nylon with platelet or spherical particles for all test temperatures [5]. Further, it was shown that ultimate tensile strength increased at all temperatures when the volume fraction of particles in the nylon system was increased (from 59.7 to 71.0%). At low and room temperatures, formulations containing platelet morphology particles were found to possess a higher ultimate tensile strength than formulations containing spherical morphology particles, while at high temperatures formulations with spherical morphology possessed a higher ultimate tensile strength than those containing an equivalent volume fraction of platelet morphology particles. Finally, for plain nylon and in the platelet morphology formulations a general trend of decreasing ultimate tensile strength with increasing temperature was followed. For the spherical morphology system, there was a decrease in ultimate tensile strength with increasing temperature from low to room temperature and an increase when increasing temperature from room to high temperature. Ultimate tensile strength values for platelet-containing nylon formulations ranged from 35–70 MPa at −40°C, 18–47 MPa at 23°C, and 1–27 MPa at 100°C. Values for the spherical containing formulation were reported to be 8, 5, and 10 MPa at −40, 23, and 100°C, respectively.

Flexural strength results were obtained at room temperature on nylon formulations containing platelet morphology particles at three volume fractions (58, 60, and 69 vol% particles) [5]. Values for flexural strength ranged from 40–55 MPa with the 60 vol% powder formulation having a lower strength than the 58 and 69 vol% formulations. Although flexural strengths were found to be higher than tensile strengths, as expected, no relation could be determined between flexural strength and particle volume fraction. The higher flexural strengths, as compared to tensile strengths, were attributed to specimen size-effects in the samples.

Four PPS formulations (ranging from 50.3 to 61.4 vol% platelet morphology particles) were also previously tested in tension [6]. Ultimate tensile strength was found to decrease with both increasing temperature and increasing volume fraction of particles with values ranging from ≈80 MPa at −40°C down to ≈10 MPa at 180°C. Tensile strength was found to decrease by more than 60% at high temperatures and was found to increase by ≈20% at low temperatures (compared to room temperature values).

Only two PPS formulations were tested in flexure (51.7 and 61.4 vol% platelet morphology particles) and testing was only performed at room temperature [6]. The formulation with the lower volume fraction of particles was found to possess a higher bending stress (85 MPa as opposed to 65 MPa) and values for both formulations were higher than those obtained at room temperature in tension. The trend of decreasing strength with increasing volume fraction of particles would be consistent with the tensile strength data. The higher magnitude flexural strengths, as compared to tensile strengths, were attributed to the same size-effects present during bending as noted for the nylon samples.

It was also demonstrated in the previous work [5] that particle morphology plays an important role in the ultimate tensile strength of the injection molded magnets. Formulations containing platelet particles were found to exhibit higher strengths (by 80% at −40°C and 90% at 23°C) than those containing similar volume fractions of spherical particles. This observation is supported by independent finite element analysis performed by Brockenbrough and Suresh [7] and by Chen *et al.* [8], which show that failure modes of composites change with various particle morphologies.

Square edged reinforcement is shown to exhibit greater resistance to plastic flow and higher strength, as compared to round edged reinforcement, when loaded perpendicular to the long axis of the reinforcement. This is due to the higher level of triaxiality and matrix plasticity due to the sharp corners in the reinforcement phase. Further, composites containing angular (platelet shaped) particles generally fail through particle fracture with secondary failure in the matrix, while composites containing spherical particles tend to fail primarily at the matrix level (through void nucleation, growth and coalescence). The reason behind this is shown to be that voids nucleate preferentially at the interface between the matrix and the particles. Therefore, in composites containing angular particles (those with edges) the reinforcement will carry a higher ratio of stress than the matrix. Alternately, in composites containing spherical particles (those without edges), the matrix will carry the higher ratio of stress compared to the reinforcement. This would result in lower strengths for magnetic materials containing spherical particles and higher strengths for magnetic materials containing platelet particles, as the plastic matrix possesses a lower strength than the metallic particles.

It has been shown that maximizing the volume fraction of powder present in the magnet formulations will optimize their magnetic properties [9]. Yet, the above data demonstrate that maximizing the volume fraction of powder present in the magnet formulations may not necessarily maximize their mechanical strengths. It is expected that there exists a critical volume fraction of powder for which values will be maximized before subsequent powder additions have an adverse affect.

This is seen in metal matrix composites [10], where improvements in toughness are associated with the ability of the material to increase its energy absorption during crack propagation. Increases in fracture toughness are achieved by engineering the interface between the secondary phase and the matrix (maximizing matrix/particulate interfacial shear strength) and by controlling the geometry of the secondary phase (particle size distribution and orientation). As the particle size is increased, the area of matrix/particulate interaction is increased along with the interfacial energy needed for crack propagation. Also, by orienting the long axis of a non-equiaxed particle perpendicular to the direction of crack propagation, an increased interfacial shear area is produced. Equally important is the spacing between particles, since particles are sources for void nucleation within the composite, which leads to a decrease in fracture toughness. This leads to the critical volume fraction of particles mentioned above. Initial particle additions will increase fracture toughness as the matrix/fiber interfacial shear strength is increased and geometric effects cause crack branching and blunting. After the critical volume fraction of secondary phase is reached, subsequent additions then reduce the fracture toughness as the distance between secondary particles decreases and there is a greater chance of void nucleation between the particles. Therefore, additional particle loading above the critical volume fraction becomes deleterious to fracture toughness.

3. Experimental

Metallic Nd-Fe-B powders (produced by Magnequench Inc., Indianapolis, Indiana) were combined with a lubricant and either Nylon-12 resin or PPS to produce finished magnets with powder volume fractions of 51–62%. Three different particles were used, two of which had platelet morphology (MQP-B and MQP-O) and one that possessed a spherical morphology (MQP-S-9-8). Differences in the MQP-B and MQP-O particles are only in their magnetic properties and not in their size or morphology. Actual formulations are listed in Table I.

A twin-screw extruder was used to produce feedstock for injection molding. Feedstock was pelletized cylindrical pieces of roughly 5 mm diameter and 3 mm thickness, which were dried to a dew point of −40°C to assure moisture removal before injection molding. Test specimens were injection molded under argon into geometries to conform to the specifications of ASTM D638-01 for tensile strength of plastics [11] and ASTM D6272-00 for flexural properties of plastics [12].

TABLE I Magnet formulations tested

Designation	Polymer type	Powder type	Particle volume fraction (%)
F	PPS	MQP-B	61
H	Nylon 12	MQP-B	58
M	Nylon 12	MQP-B	69
V	PPS	MQP-O	61
W	PPS	MQP-B	51
X	PPS	MQP-O	51
Y	Nylon 12	MQP-B	60
ZK	Nylon 12	MQP-S-9-8	62
9-8/PA A1	Nylon 12	MQP-S-9-8	60

Note. MQP-B and MQP-O are powders containing platelet morphology particulates with similar particle sizes, but varying magnetic properties; MQP-S-9-8 is a powder containing spherical morphology particulates.

As produced specimens were then subjected to thermal cycling between −40 and 150°C in an environmental chamber (ATS series 3700) with both active heating through the use of resistance heating elements and active cooling through the use of liquid nitrogen. Specimens were held in place and suspended in the chamber by a series of metal springs. Heating rates were on the order of 7°C/min, while cooling rates were on the order of 10°C/min, with a complete cycle taking approximately 45 min. The temperature within the chamber was monitored using three vertically mounted type-K thermocouples with the furnace being controlled by a controller (ATS series 3000) using the thermocouple located in the middle of the furnace for feedback. Samples were subjected to 50, 500, or 5000 cycles prior to mechanical testing.

Tensile testing was performed at room temperature using an electromechanical testing machine with computerized data acquisition in accordance with ASTM D638-01 [11]. Samples were dog-bone shaped standard type-IV specimens with a rectangular cross section of 3.2 × 6.0 mm. The specimens were 115 mm in total length with a 25 mm test section gauge length and were injected in the direction of mechanical loading. Tests were conducted at a constant speed of 5 mm/min. on material formulations F, H, V, W, X, Y, ZK, and 9-8/PA A1 as given in Table I. The engineering stress was determined during each test by dividing the applied force by the original cross-sectional area of the sample. Engineering strain was determined by contact extensometry.

Flexure testing was also performed at room temperature using an electromechanical testing machine with computerized data acquisition in accordance with ASTM D6272-00 [12]. Samples were 127 × 12.7 × 6.4 mm rectangular bars with the direction of injection perpendicular to the loading direction. Tests were conducted at a constant speed of 5 mm/min. in 4-point loading using a stainless steel fixture with a loading span of 38.1 mm and a support span of 76.2 mm. Testing was performed on material formulations F, H, M, W, and Y as given in Table I. Flexural bending strengths were calculated using the following equation:

$$S = \frac{3PL}{4bd^2} \tag{1}$$

where S = flexural bending strength, P = breaking load, L = outer (support) span, b = specimen width, and d = specimen thickness.

Statistical analysis at a 95% confidence interval was performed on all data (unless otherwise noted) to determine if differences observed between different experimental conditions were significant. Comparisons were made between nylon and PPS formulations, different powder types, different numbers of thermal cycles within a formulation, and different powder volume fractions.

Fractured surfaces from both tensile and flexural testing were characterized using optical microscopy

(OM) and scanning electron microscopy (SEM). Selected NyY specimens in the un-cycled state and after 50 and 5000 cycles were analyzed using dynamic mechanical analysis (DMA) using a TA Instruments Model Q800 DMA.

4. Results

Thermal cycling produced some noticeable physical effects on the bonded magnets. Corrosion was seen on the surface of some samples and is thought to be related to the condensation of water vapor and subsequent oxidation of the sample surface during the cooling segments of thermal cycling. The corrosion product is expected to be red-brown rust (consisting of Fe_3O_4, Nd_2O_3, α-Fe_2O_3, and cubic Fe_2O_3) as previously noted for the corrosion of Nd-Fe-B compounds by Hua *et al.* [13]. Similar discoloration of nylon surfaces was also observed. As would be expected, the severity of this effect increased with the number of cycles.

Mechanical behavior of polymeric materials in tension is classified by Moore and Kline [14] into four general types. These general classes of behavior are (1) low modulus/low strength/low toughness, (2) high modulus/high strength/low toughness, (3) high modulus/high strength/high toughness, and (4) low modulus/high strength/high toughness as shown in Fig. 1 with the modulus being given by the slope of the initial linear segment and the toughness estimated by the total area under the stress-strain curve. Therefore, the results from mechanical testing in tension were analyzed in regard to modulus, strength, and toughness as deduced from the experimentally determined engineering stress-strain curves. Results from the testing are presented in Table II.

Characteristic engineering stress-strain curves for cycled nylon and PPS based magnets in tension are shown in Figs 2 and 3, respectively. In most cases 2-3 samples were tested under each condition and results were averaged. As a whole, the nylon-based magnet formulations showed higher toughness, lower modulus, and lower strengths than the PPS based magnet formulations. This was largely due to a higher degree of ductility being exhibited by the nylon-based materials.

Curves for the two nylon formulations containing platelet morphology particles are shown in Fig. 2a, with failure strain values on the order of 0.1–0.9%. It was found that the formulation containing the lower powder volume fraction (58%) exhibited higher strength and a higher modulus than the formulation containing 60 vol% powder. Thermal cycling was seen to have a limited effect on the strength of the 60 vol% powder formulation (abbreviated as vol% formulation for the remainder of this paper), but a decrease in toughness was seen with increased number of cycles. A small decrease in toughness was seen between samples cycled 50 and 500 times due to a decrease in sample ductility. Comparatively, a large increase in ductility and a corresponding

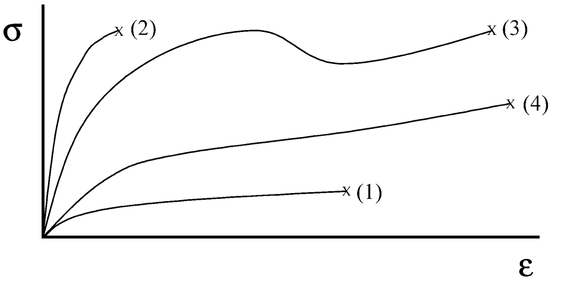
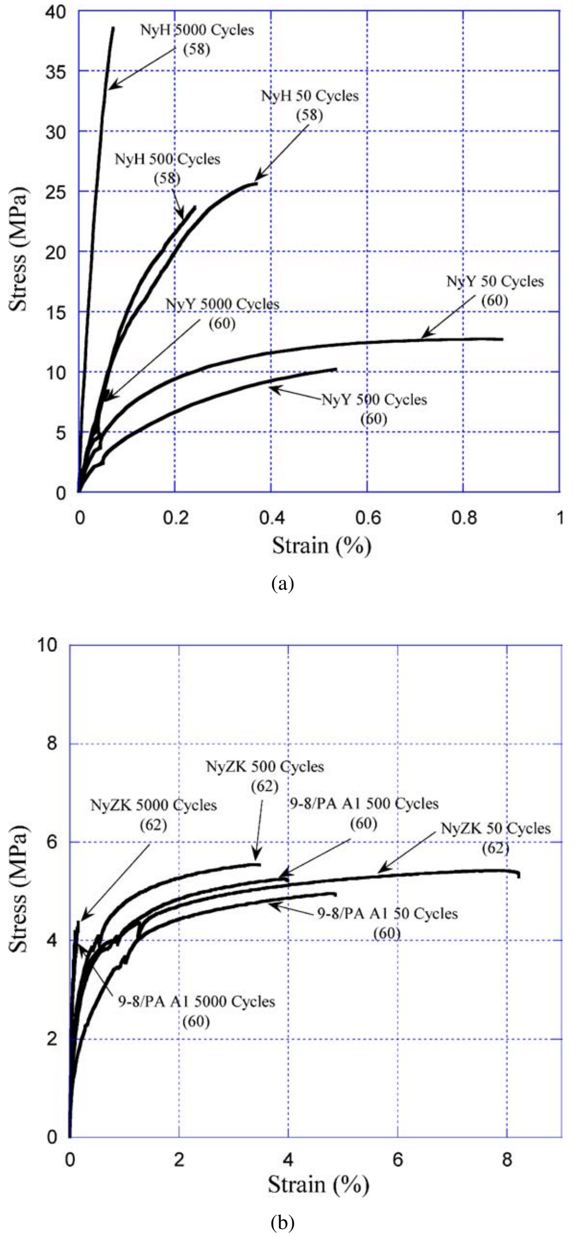


Figure 1 General types of behavior exhibited by polymers in tension.

TABLE II Numerical results from testing

Formulation (cycles)	Modulus (MPa)	Strength (MPa)	Toughness (MJ/m^3)
A. Tensile results			
Nylon H			
50	136.94	24.25	6.42
500	156.38	25.93	3.60
5000	880.33	35.79	1.65
Nylon Y			
50	104.68	12.57	9.34
500	72.70	12.16	3.76
5000	213.56	10.36	0.309
Nylon ZK			
50	16.21	4.82	40.20
500	14.85	4.95	16.80
5000	76.14	3.9	0.276
Nylon 9-8			
50	24.18	5.14	20.33
500	17.90	4.94	18.03
5000	73.83	4.24	0.484
PPS F			
50	227.50	29.56	4.64
500	238.46	42.31	6.67
5000	968.29	37.65	0.825
PPS V			
50	172.80	30.19	2.96
500	281.47	32.89	2.47
5000	783.39	33.31	0.721
PPS W			
50	273.27	64.81	12.79
500	233.91	64.10	13.03
5000	968.77	71.66	4.11
PPS X			
50	270.73	57.85	6.85
500	220.33	72.86	14.60
5000	946.27	75.29	4.87
B. Flexural results			
Nylon H			
50	67.75	47.46	29.91
500	82.90	48.12	25.54
5000	88.03	54.14	22.50
Nylon M			
50	116.57	40.61	5.50
500	125.43	49.16	10.77
5000	127.9	38.21	7.56
Nylon Y			
50	40.15	16.96	3.72
500	44.80	19.88	4.90
5000	41.14	21.56	8.07
PPS F			
500	115.23	64.46	16.12
5000	126.05	64.49	14.81
PPS W			
50	118.43	109.26	51.64
500	114.32	105.08	45.82
5000	123.17	107.27	50.17

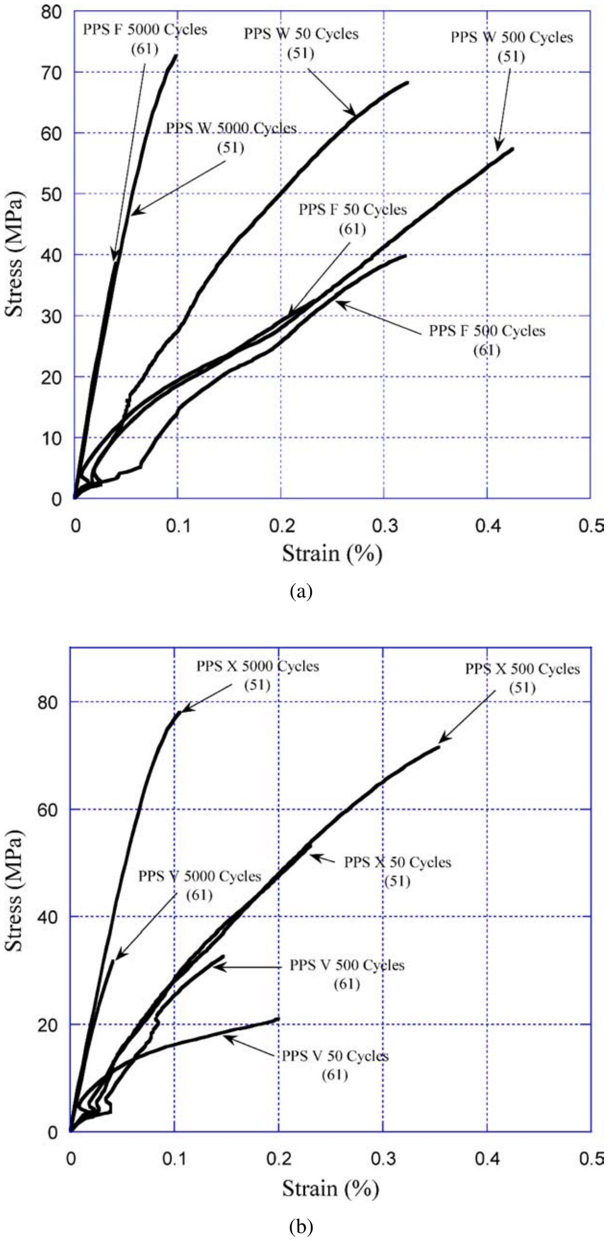
Note. Modulus based on slope of initial linear portion of stress/ displacement curve. Toughness based on area beneath stress/ displacement curve.



(a)

(b)

Figure 2 Characteristic tensile stress-strain curves for nylon magnet formulations.



(a)

(b)

Figure 3 Characteristic tensile stress-strain curves for PPS magnet formulations.

increase in modulus was seen in samples cycled for 5000 cycles resulting in a large decrease in toughness. The 58% formulation showed little change in strength for samples cycled 50 and 500 times, but an increase in both strength and modulus when cycled for 5000 repetitions (strength increased ≈30% from the value exhibited after 50 and 500 cycles). The same decrease in toughness due to a decrease in ductility for the lower number of cycles as seen above was also evident for this formulation. Additionally, as compared to the formulations containing spherical morphology particles (discussed below), the platelet morphology formulations exhibited much higher strengths (greater by 100–400%), higher modulus, and much lower toughness.

Fig. 2b shows the curves for the nylon formulations containing spherical morphology particles, with failure strain values on the order of 0.1–8%. Both the 60 and 62 vol% formulations showed similar strengths, toughness, and modulus values. As seen for the platelet containing formulations, thermal cycling resulted in a moderate decrease in toughness between samples cycled 50 and 500 times, and a large decreases in toughness after 5000 cycles. For the 60 vol% formulation, the decreases in toughness were due to a loss of ductility and a corresponding increase in modulus in the samples with increased number of thermal cycles. The 62 vol% formulation showed an initial decrease in toughness between samples cycled 50 and 500 times due to a decrease in sample ductility, and a large decrease in toughness after 5000 cycles due to a decrease in ductility and a corresponding increase in modulus as seen for the other formulations. Toughness values from tensile testing of the thermally cycled nylon based magnets are summarized in Fig. 4.

Tensile stress-strain curves for the two PPS formulations containing the MQP-B powder type are shown in Fig. 3a, with failure strain values on the order of 0.05–0.4%. The formulation containing the lower powder

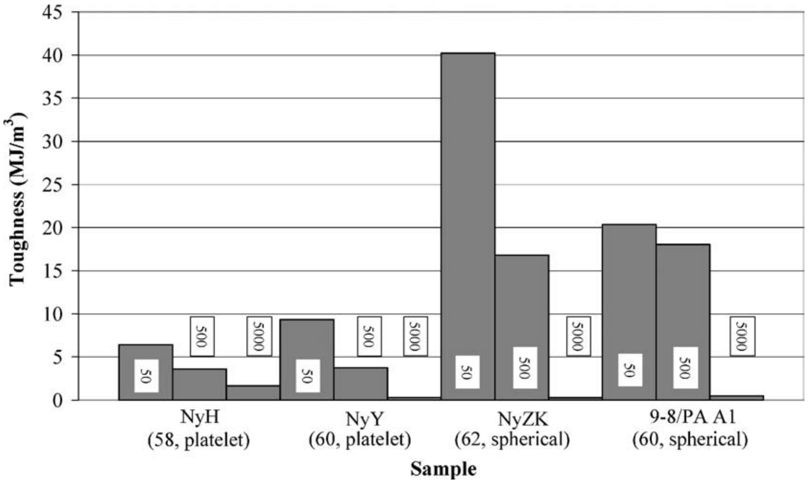


Figure 4 Tensile testing toughness results for nylon magnet formulations.

volume fraction (51%) exhibited a similar modulus, but higher strength than the formulation containing 61 vol% powder. Strength of the 51 vol% formulation was relatively unchanged by thermal cycling, while the 61 vol% formulation showed a slight increase in strength between samples cycled 50 times and those cycled for 500 and 5000 times. This resulted in an increase in toughness between samples cycled for 50 and 500 times for the 61 vol% formulation. After 5000 thermal cycles, both formulations showed a decrease in ductility and a corresponding large increase in modulus leading to a large decrease in toughness (as seen for the nylon formulations).

Fig. 3b shows the curves for PPS formulations containing the MQP-O powder type, with failure strain values again on the order of 0.05–0.35%. The 51 vol%

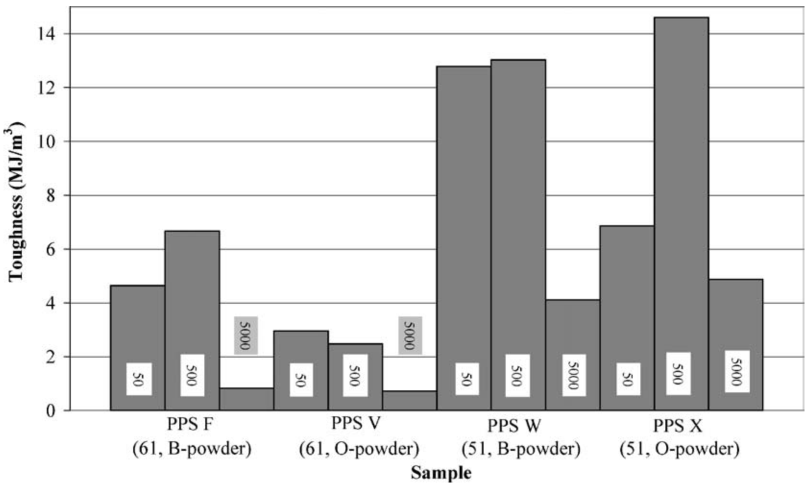


Figure 5 Tensile testing toughness results for PPS magnet formulations.

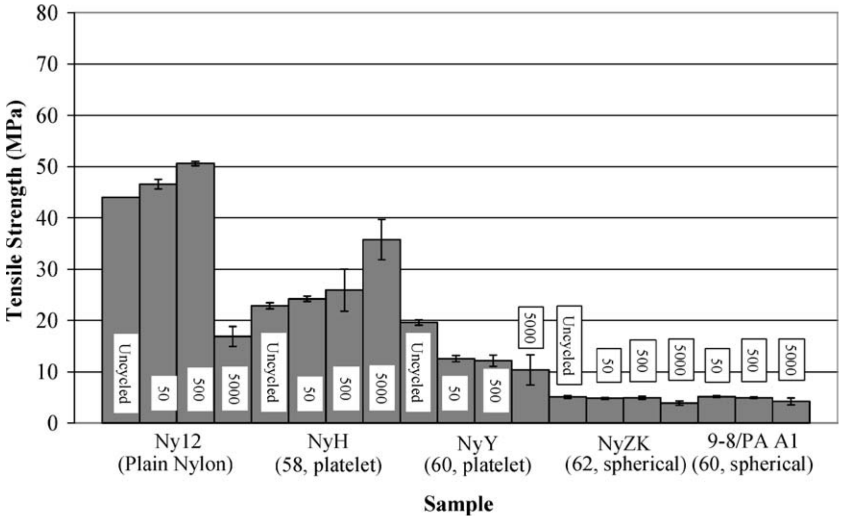


Figure 6 Tensile testing strength results for nylon magnet formulations.

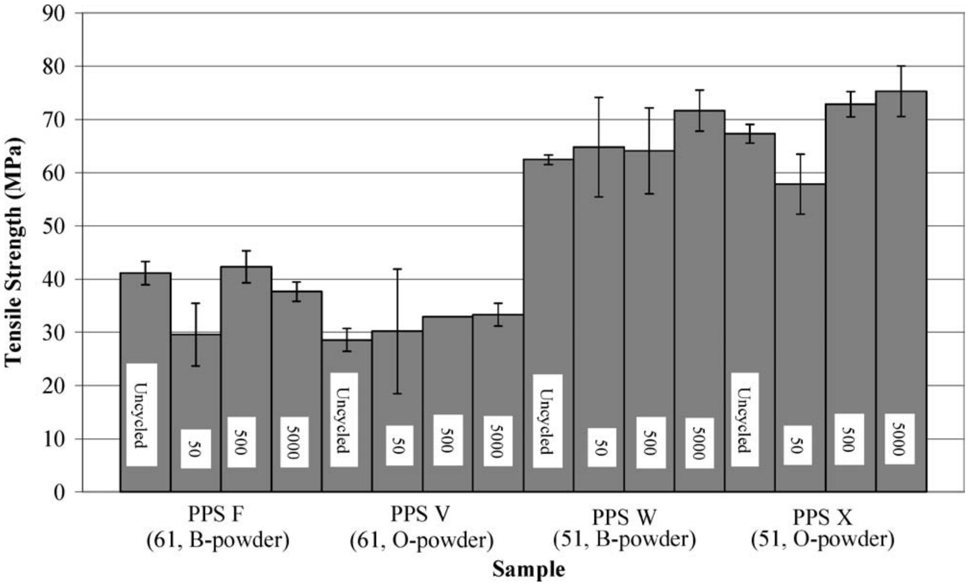


Figure 7 Tensile testing strength results for PPS magnet formulations.

formulation again displayed a higher strength than the 61 vol% formulation at all levels of thermal cycling and a greater toughness, while modulus values were equivalent for the two formulations. For the 51 vol% formulation, strength increased between samples thermally cycled 50 and 500 times and a subsequent increase in toughness was seen. The 61 vol% formulation showed no differences between samples cycled 50 and 500 times. Similar to the behavior described previously, a large increase in modulus was seen for samples of both formulations cycled 5000 times, which led to a corresponding large decrease in toughness. Toughness values from tensile testing of the thermally cycled PPS based magnets are summarized in Fig. 5.

Strength results from tensile testing of the thermally cycled nylon and PPS based magnets are summarized in Figs 6 and 7, respectively along with data from uncycled materials. Values shown are an average of 2–3 samples.

As reported previously, pure nylon (Ny12) possessed a higher tensile strength than the nylon formulations containing magnet powders in both the uncycled and 50 to 500 cycled states (by ≈50% in the uncycled state for platelet morphology particles and ≈90% for spherical morphology particles in the uncycled state). Tensile strength values for pure nylon were on the order of 40–50 MPa, while composite values ranged between 5–35 MPa. While a slight increase in strength was seen for plain nylon samples thermally cycled 50 or 500 times, a sharp decrease in strength was seen for samples cycled 5000 times. This made the strength of plain nylon samples more equivalent to those of the nylon formulations containing particles for samples thermally cycled 5000 times. Further, as mentioned earlier, formulations containing platelet morphology particles (NyH and NyY) showed a statistically higher ultimate tensile strength than those containing spherical particles (NyZK and 9-8/PA A1) regardless of thermal cycling.

For the nylon formulations containing platelet morphology particles, there was a statistically significant decrease (≈50%) in tensile strength of the thermally cycled samples with a 2% increase in particle volume fraction (from 58–60 vol% particles). The lower volume fraction formulation appeared to increase in tensile strength with increasing number of thermal cycles, but the amount of increase was found to fall within the standard deviation of the data for the 50 and 500 cycled samples. The 5000 cycled samples though, showed a significant increase in strength over the uncycled material. All three of the thermally cycled samples for the higher volume fraction formulation showed comparable tensile strengths, but significantly lower (≈40%) tensile strengths than uncycled samples.

For the nylon formulations containing spherical morphology particles, there was no discernable difference in ultimate tensile strength between formulations containing 60 and 62 vol% powder. Further, there appeared to be no effect on strength in these samples due to thermal cycling. All samples possessed low strengths of approximately 5 MPa.

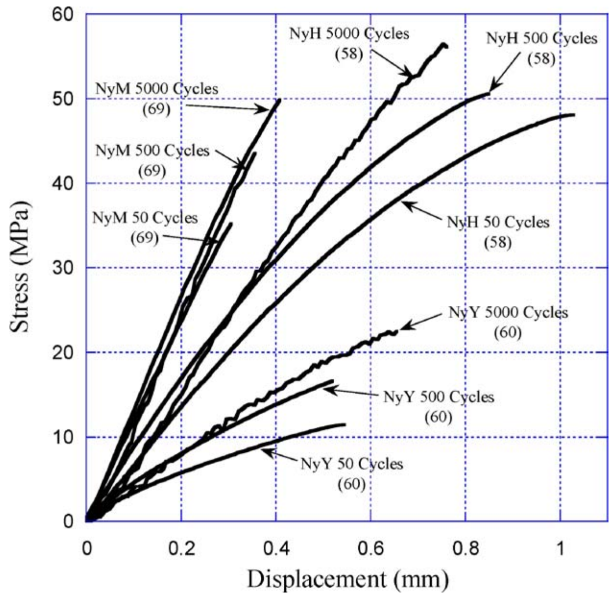


Figure 8 Characteristic flexural stress versus cross-head displacement curves for nylon magnet formulations.

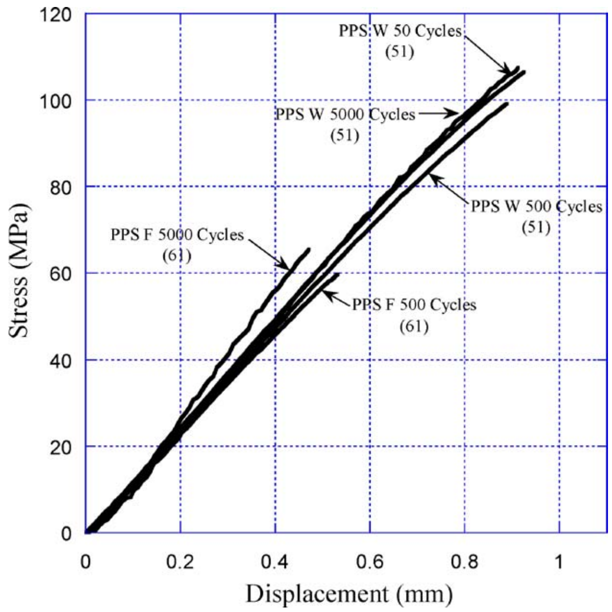


Figure 9 Characteristic flexural stress versus cross-head displacement curves for PPS magnet formulations.

The PPS formulations containing the lower volume fraction of powder (51%) exhibited a statistically significantly higher (≈45%) ultimate tensile strength than those containing a higher volume fraction of powder (61%). Further, with the exception of 50 cycle formulation F condition, which showed ≈25% reduced ultimate tensile strength, no significant effect on strength was determined due to cycling of 50 or 500 times in formulations F, V, and W. Yet, there was a significant effect in these formulations after 5000 thermal cycles with formulation F showing a decrease in strength (8.5%) and formulations V and W showing increases in strength (14 and 13%, respectively). Formulation X also showed significant differences between samples cycled for 50 and 500 cycles and for 50 and 5000 cycles (at a 90% confidence level). For this formulation, the 50 cycle samples showed reduced (≈15%) ultimate tensile strength compared to the uncycled samples, while the 500 and 5000 cycle samples showed increased ultimate tensile strength compared to both the uncycled and 50 cycle samples.

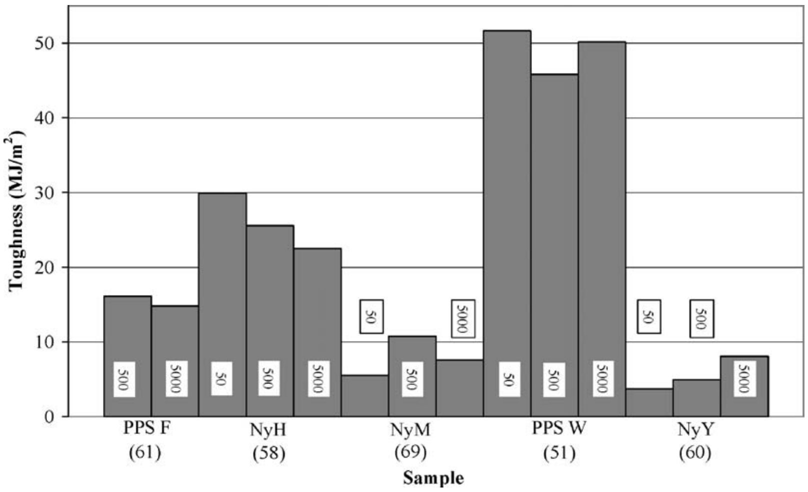


Figure 10 Flexure testing toughness results for nylon and PPS magnet formulations.

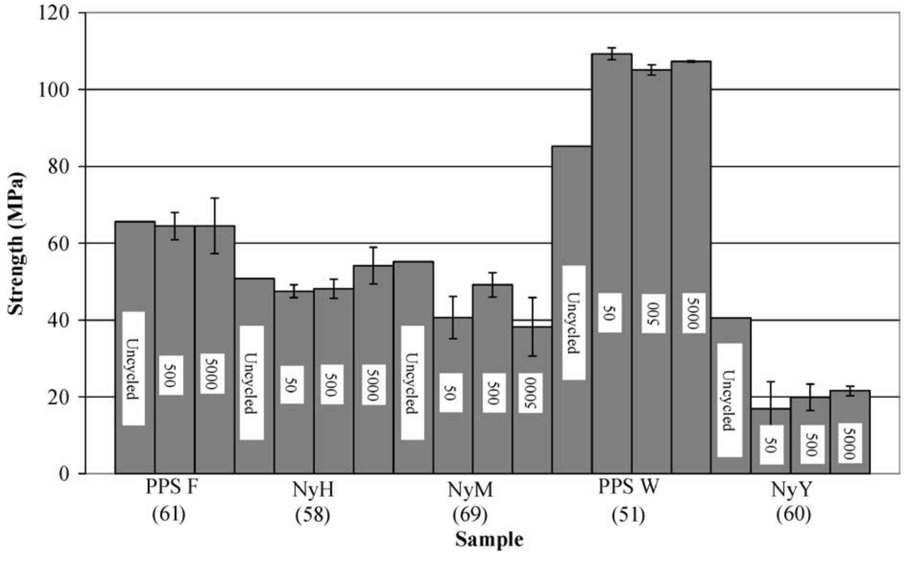


Figure 11 Flexure testing strength results for nylon and PPS magnet formulations.

No correlation could be drawn between the strength values and the type of magnet powder used (MQP-B vs. MZP-O). Since MQP-B and. MZP-O powders are the same powder morphology and nearly identical particle size distribution, one would not expect any difference in mechanical strength values for the same polymer matrix and identical volume fraction formulations, provided that the surface chemistry of the powders is the same. As mentioned earlier, all PPS formulations showed a higher ultimate tensile strength than those exhibited by the nylon formulations, although pure nylon possessed similar strength properties to those of the PPS formulations.

Characteristic flexural stress vs. cross-head displacement curves for cycled nylon and PPS based magnets are shown in Figs 8 and 9, respectively. In most cases 2–3 samples were tested under each condition and results were averaged. Results were compared against the previously referenced 4 model types of behavior described by Moore and Kline [14] for polymeric materials in tension. Overall, the PPS based materials showed higher

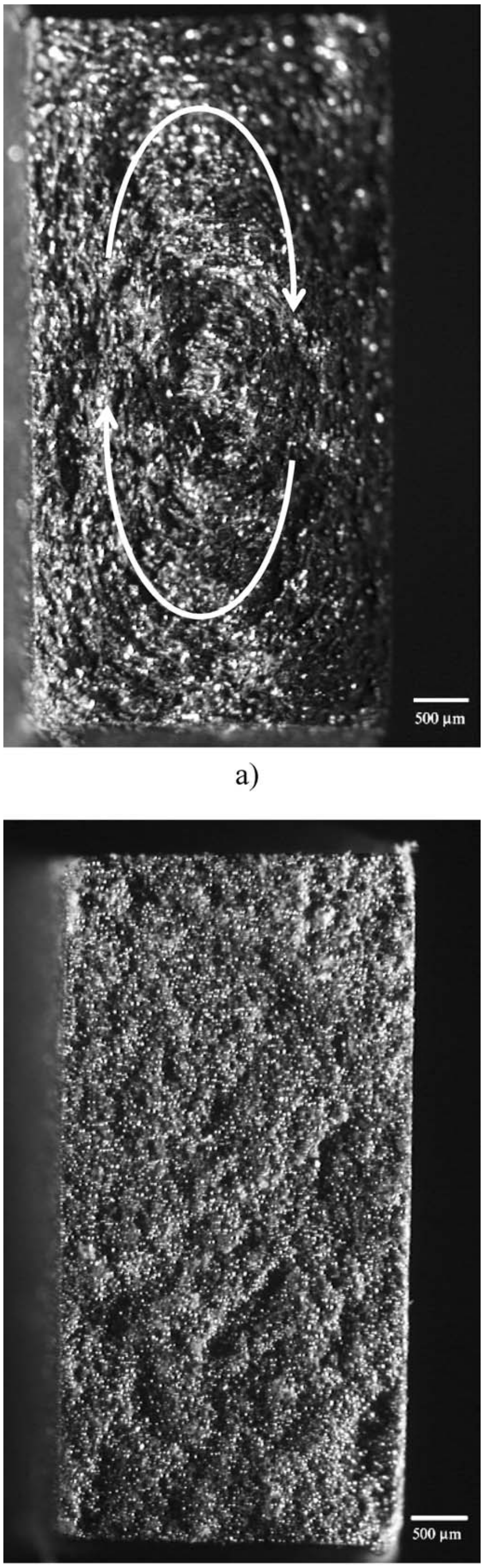


Figure 12 Optical micrographs of tensile fractured surfaces from nylon magnets with: (a) platelet morphology and (b) spherical morphology.

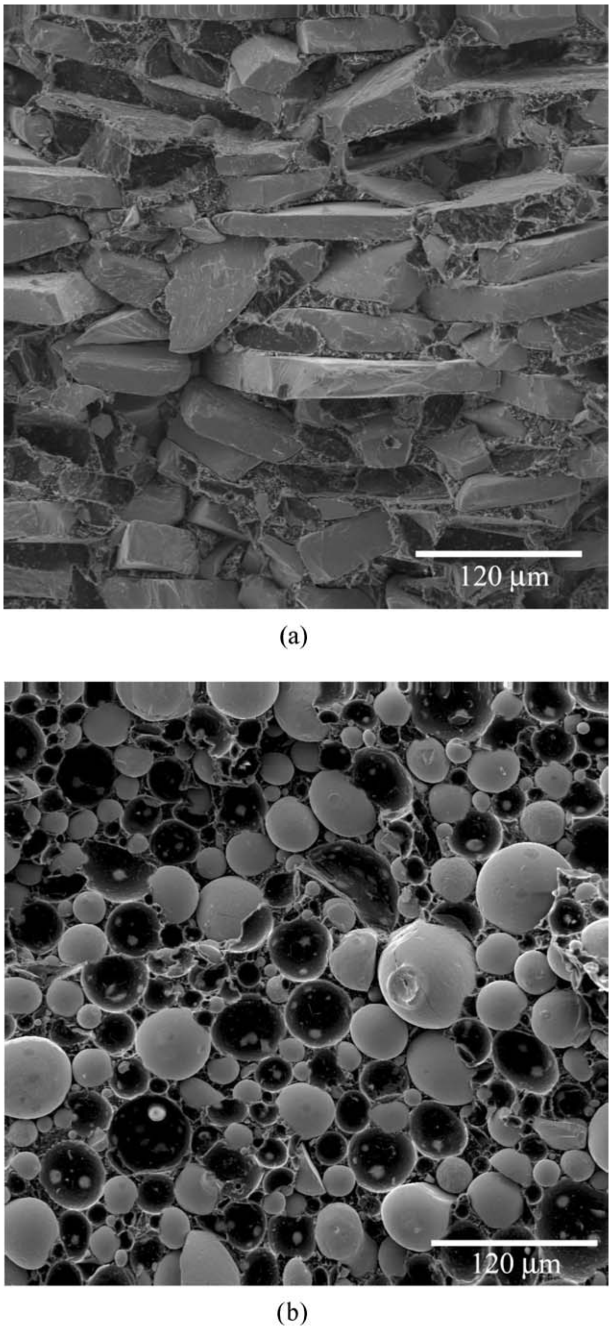
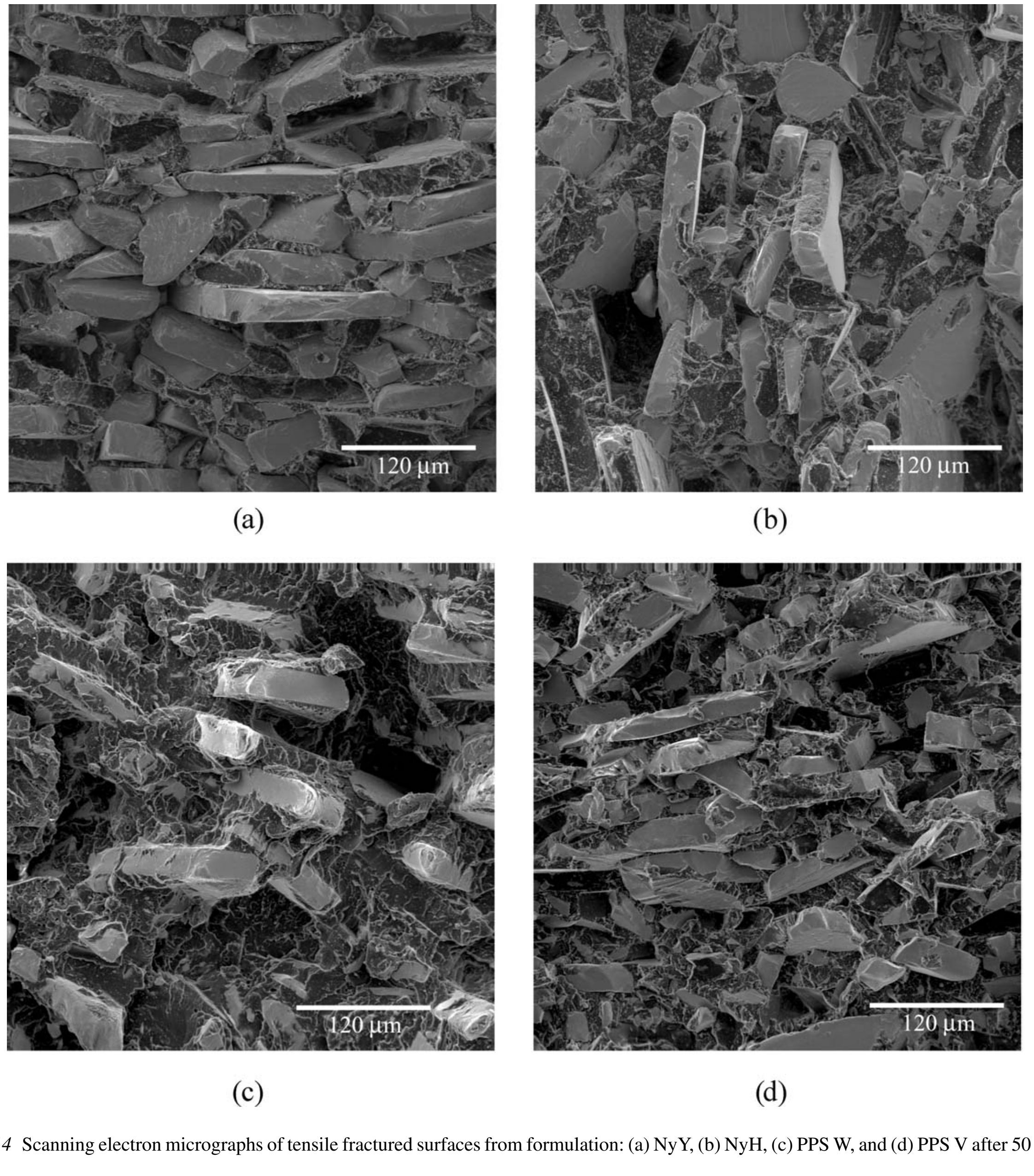


Figure 13 Scanning electron micrographs of tensile fractured surfaces from nylon magnets with: (a) platelet morphology and (b) spherical morphology.

strength and modulus values than the nylon based magnets in flexure. This resulted in higher toughness values for the PPS based materials.

Flexural stress-displacement curves for the three tested nylon formulations are shown in Fig. 8, with all formulations containing the platelet morphology particles. Displacement values were on the order of 0.3–1.0 mm, with the formulation containing the lowest powder volume fraction (58%) exhibiting the highest amount of displacement and the formulation containing the highest powder volume fraction (69%) exhibiting the lowest amount of displacement. The formulation containing 60 vol% powder exhibited an intermediate level of displacement approximately halfway between the levels of the other two formulations. For the 58 vol% formulation, modulus values increased with increasing number of thermal cycles, while modulus values were relatively unchanged by thermal cycling for the 60 and 69 vol% formulations. Toughness gradually decreased with increased thermal cycling for the low volume fraction (58%) formulation due to the increases in modulus values and a decrease in ductility. Toughness values were similar for the 60 vol% formulation after 50 and 500 thermal cycles, but an increase in toughness was seen after 5000 thermal cycles due to an increase in sample ductility (higher displacement). For the high volume fraction (69%) formulation, an increase in toughness was seen between samples thermally cycled for 50 and 500 times due to an increase in strength, but a decrease was seen between samples thermally cycled 500 and 5000 times due to a decrease in strength.

Fig. 9 shows flexural stress versus displacement curves for the two tested PPS formulations with displacement values on the order of 0.4–0.9 mm. The formulation containing 51 vol% powder showed higher strength and toughness than the formulation containing 61 vol% powder, but modulus values were similar for both formulations. Negligible changes in strength, modulus, or toughness were seen in either formulation due to thermal cycling.



(a) (b) (c) (d)

Figure 14 Scanning electron micrographs of tensile fractured surfaces from formulation: (a) NyY, (b) NyH, (c) PPS W, and (d) PPS V after 50 thermal cycles.

Toughness values resulting from flexure testing of cycled nylon and PPS based magenets are summarized in Fig. 10. Strength Results from flexure testing of cycled nylon and PPS based magnets are summarized in Fig. 11, along with data from uncycled materials. In most cases 2–3 samples were tested under each condition and average values were calculated.

Strength values were found to range from 17–110 MPa, with values for all formulations being higher in flexure than those seen in tension. The higher magnitude flexural strengths, as compared to tensile strengths, were attributed to the same size-effects present during bending as noted previously.

The two tested PPS formulations (F and W) both exhibited statistically significantly higher flexural strengths than the three tested nylon formulations (H, M, and Y). Differences in strength, of as much as 80%, were seen between PPS and nylon formulations. Further, the lower volume fraction (51%) PPS formulation showed statistically significantly higher strength than that of the higher volume fraction (61%) PPS formulation, with the difference in strength on the order of 40%. Thermal cycling for 500 and 5000 cycles did not appear to have a significant effect on the PPS F formulation, but testing was not performed on samples cycled for only 50 cycles as done in tension (50 and 5000 cycle tension samples showed a significant decrease in strength while 500 cycle tension samples displayed equivalent strength to uncycled samples as discussed above). A significant increase (≈20%) was seen between cycled and uncycled samples of the PPS W formulation and a significant difference at a 90% confidence level (≈4% decrease) was seen between samples cycled 50 and 500 times, but not between samples cycled 50 and 5000 times nor between samples cycled 500 and 5000 times.

The nylon formulations containing 58 and 69 vol% powder (H and M) exhibited similar flexural strengths and showed no significant effect of thermal cycling. Yet, the 60 vol% nylon formulation (Y) showed a statistically significantly lower flexural strength (by 58%) and a significant decrease in strength due to thermal cycling (by 50%). No meaningful difference was seen between samples cycled 50, 500, and 5000 times.

Both optical microscopy and scanning electron microscopy (SEM) were performed on tensile fractured surfaces of nylon-based samples containing platelet morphology particles and spherical morphology particles. Characteristic images from the optical analysis are shown in Fig. 12 while SEM images are shown in Fig. 13. Overall, the fractured surfaces of the formulations containing platelet morphology particles were found to have a larger particle size and to show less particle pullout than those containing spherical particles. Additionally, the platelet morphology particles aligned themselves in concentric rings emanating from the center of the specimen (thought to be due to the injection molding process), while the spherical particles were distributed randomly showing no such alignment.

Further SEM was performed on both nylon and PPS based tensile specimens exhibiting the extreme values of strength and ductility. Fig. 14 shows micrographs of formulations NyY (high ductility/low strength), NyH (low ductility/high strength), PPS W (high ductility/high strength), and PPS V (low ductility/low strength) after 50 thermal cycles.

Several differences were seen between the two nylon-based samples. First, the NyY sample shows higher levels of particle pullout than that seen for the NyH sample. Additionally, the NyH sample has broken particles visible in the micrograph, while the particles seen in the NyY micrograph are all whole.

Yet, the two nylon based materials both appear to have less intimate bonding between the particles and the matrix than seen in the two PPS based materials. In Fig. 15a the PPS matrix can be seen surrounding the particle embedded within it. Such behavior was not seen for the nylon formulations, which showed much "cleaner" particle surfaces (as shown in Fig. 15b).

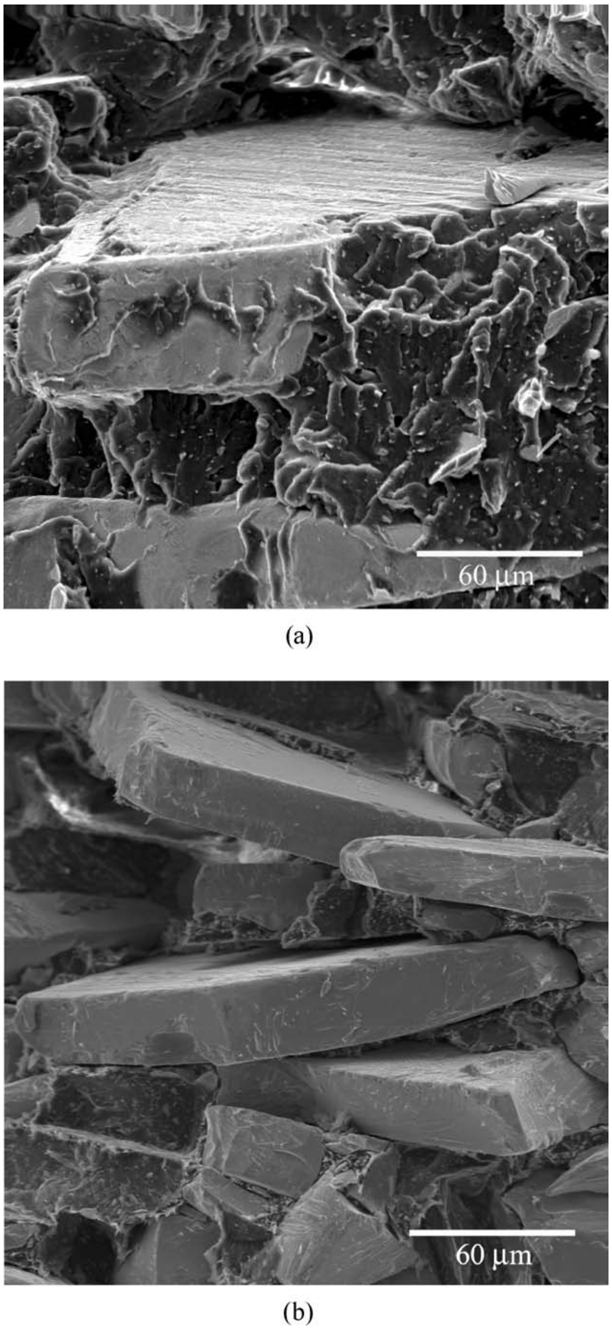


Figure 15 Scanning electron micrographs of particle/matrix interaction in tensile fractured surfaces from formulation: (a) PPS W and (b) NyY.

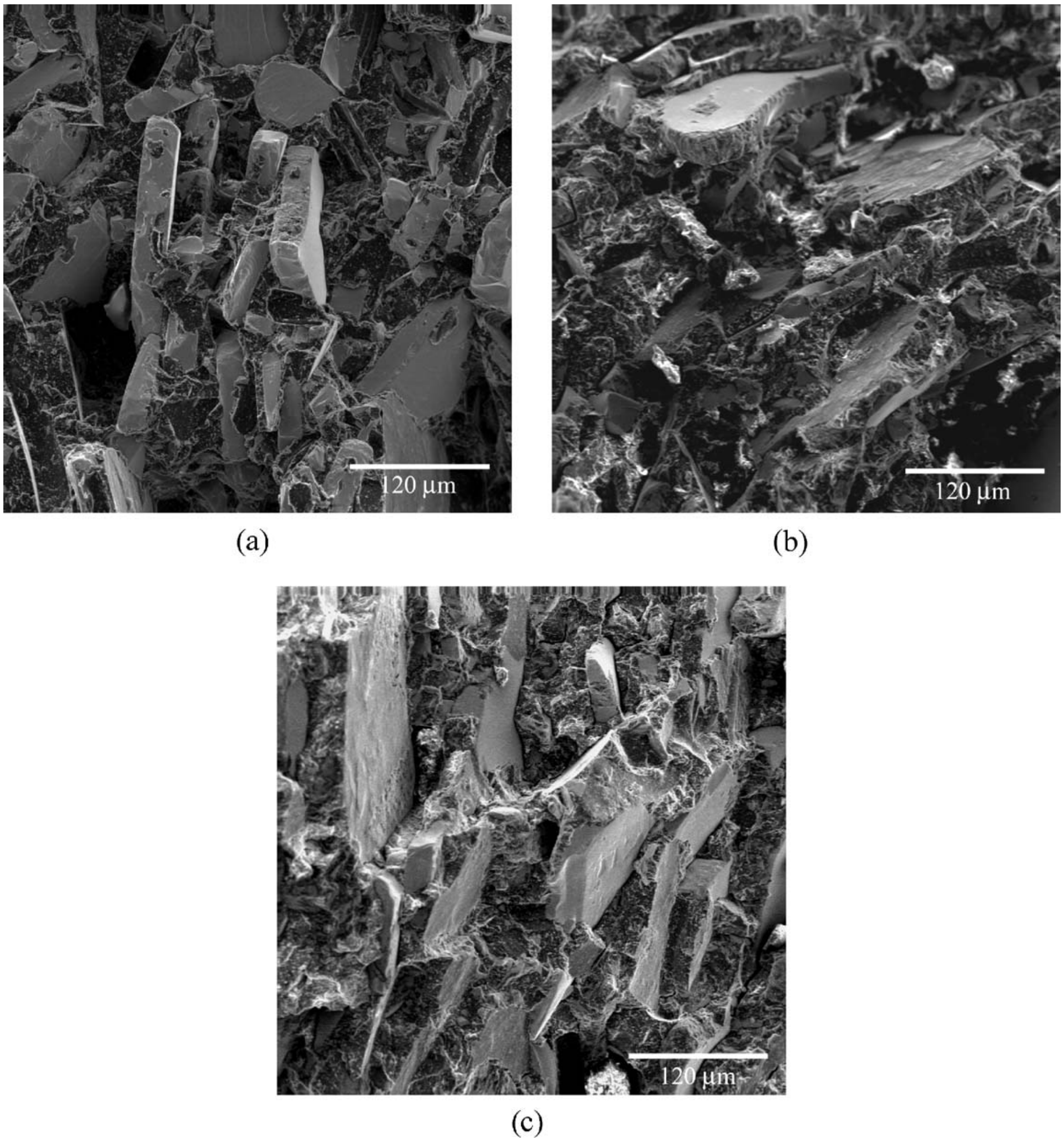


Figure 16 Scanning electron micrographs of tensile fractured surfaces from formulation NyH after: (a) 50 thermal cycles, (b) 500 cycles, and (c) 5000 cycles.

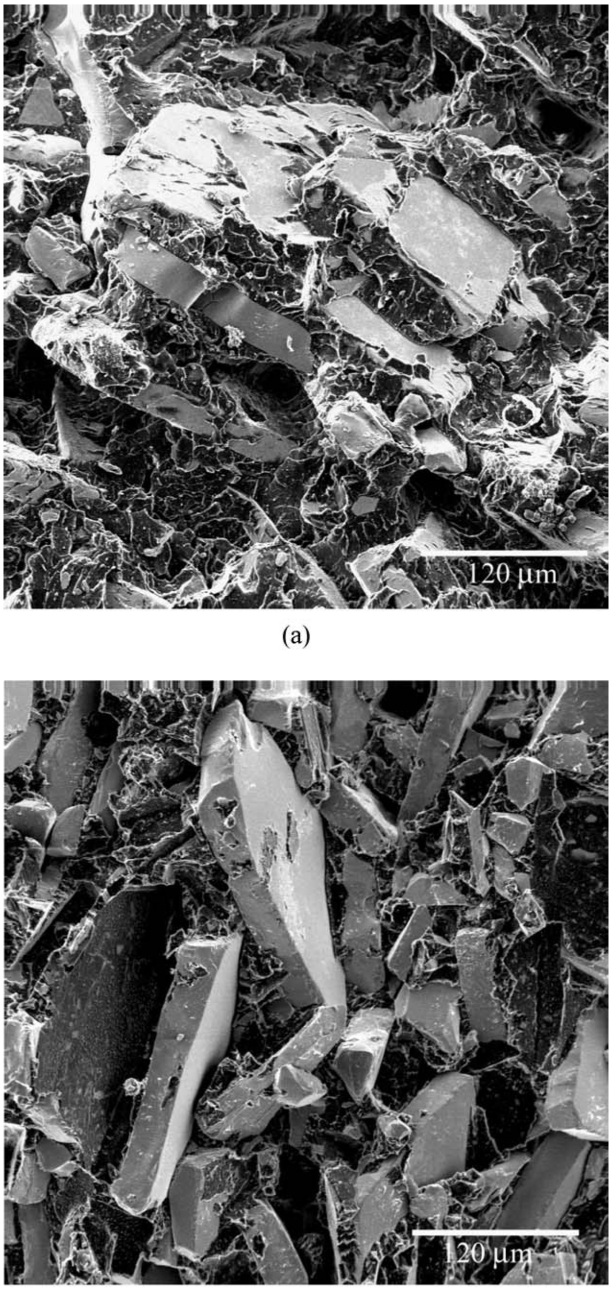
Differences were also evident between the two PPS based materials. Though they both showed higher levels of contact between the particles and matrix than that seen for the nylon based materials, the particle surfaces for the PPS V formulation appeared cleaner than those for the PPS W formulation and more particle pullout was seen for the PPS V formulation as compared to the PPS W formulation (as seen in Fig. 14c and d).

Micrographs of formulation NyH after 50, 500 and 5000 thermal cycles are shown in Fig. 16. As was typical for all samples, despite differences in strength there was not much visual difference between samples cycled for the various numbers of cycles.

SEM images from nylon and PPS based flexure samples are shown in Fig. 17. These samples showed similar behavior to that seen in tension. The matrix covers the particle surfaces in the PPS based formulation (Fig. 17a), while the particles in the nylon based formulation appear cleaner (Fig. 17b). Further, there is more evidence of particle pull out in the nylon based material than in the PPS based material.

One possible mechanism which could be responsible for the toughness/modulus changes with thermal cycling is oxidative degradation of the polymer matrix [14]. This occurs when polymer materials are subjected to heat or ultraviolet radiation in the presence of oxygen as hydrogen atoms that share a carbon atom with either a branch on a polyethylene molecule or a methyl group are attacked. Such hydrogen atoms exist in the structures of Nylon 12 and PPS. This degradation can then cause cross-linking in the polymer which leads to embrittlement, an increased glass transition temperature, an increased modulus, possible increased strength, and decreased ductility.

Raman Spectroscopy, differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA) were performed on selected specimens, representing both cycled and un-cycled conditions, to gain an understanding of structural changes occurring in these materials which may lead to the changes in mechanical properties that were discussed above. Noticeable changes in structure could not be distinguished using



(a)

(b)

Figure 17 Scanning electron micrographs of flexural fractured surfaces from formulations: (a) PPS W and (b) NyY After 50 thermal cycles.

the Raman and DSC techniques. While the DMA technique did yield some information, the results from these tests were not conclusive.

DMA analysis was performed on nylon material in the un-cycled state and after 50 and 5000 thermal cycles. The un-cycled specimen and the specimen subjected to 50 thermal cycles showed similar behavior, with the presence of a glass transition temperature at a temperature around 50–55°C. Further, a second relaxation appears to occur for these two samples at a temperature around 145°C for the un-cycled material and around 130°C for the 50 cycle material. The specimen subjected to 5000 thermal cycles showed different behavior from the other two specimens with no well defined glass transition temperature and the onset of the second relaxation event appearing at a temperature greater than 160°C. Therefore, the expected definite shifting of the glass transition temperature with increased number of thermal cycles was not readily observed. Further, a decrease in both the Loss and Storage Moduli were seen in the DMA data for materials with an increasing number of thermal cycles. This is contradictory to what would be expected based on the experimentally measured mechanical testing data presented in this paper.

5. Conclusions

It was previously shown that plain nylon is stronger in tension than nylon composited with Nd-Fe-B particles (regardless of particle morphology). Current testing supports this finding and extends it to being applicable to thermally cycled materials as well. Additionally, it was found that thermal cycling increases the strength of pure nylon. Nylon based magnet formulations were found to possess higher toughness, lower modulus values, and lower strengths than PPS based magnets in tension. Overall, little difference was seen in the mechanical properties of the PPS formulations composed of the two different powder types.

Formulations containing platelet shaped particles were found to produce stronger, higher modulus magnets, which were less tough than those containing spherical shaped particles. This is attributed to the higher level of triaxiality and matrix plasticity due to the sharp corners of this geometry. Further, composites with platelet shaped particles are expected to fail through particle fracture, while composites containing spherical particles are expected to fail at the weaker matrix level (through void nucleation, growth and coalescence) as previously discussed. This was consistent with fractographic analysis using scanning electron microscopy.

It was also found that at the levels examined in this work, increases in particle volume fraction caused decreases in both tensile strength and modulus for both nylon and PPS materials. This is in contrast to previous testing which found tensile strengths of nylon composites containing both particle morphologies to increase with increased volume fractions of powder (from 59–71% powder). Both nylon and PPS formulations in flexure showed a decrease in strength with increasing powder volume fraction, while modulus values in flexure were found to increase with increasing powder volume fraction for the nylon formulations and to remain relatively the same for the PPS formulations and toughness values in flexure were found to decrease with increasing powder volume fraction for both nylon and PPS formulations. Thermal cycling was found to have mixed effects on the strength of the nylon and PPS formulations, but was found to decrease the fracture toughness of both types of materials as evident by the total area beneath the stress-strain curves.

The observed decrease in strength with increased powder volume fraction seen in both tension and flexure is thought to be caused by the increase in the probability of void formation at the particle surfaces with the increased amount of particle surface area. It is at these voids that fracture will occur in the matrix making failure more likely as the amount of particles increases. The SEM analysis of the fractured surfaces leads to the conclusion that there differences in bonding between the particles and the matrix lead to the differences in properties seen between the various Nylon and PPS compositions.

Only minor changes in the DMA curves were evident between samples of un-cycled material and material thermally cycled 50 times. More substantial changes were seen between these materials and a material cycled 5000 times, but the expected definite shifting of the glass transition temperature with increased number of thermal cycles was not readily observed. The disappearance of the glass transition temperature for the 5000 cycle sample may be caused by crystallization occurring in this sample due to thermal exposure. This would lead to the glass transition event becoming diffuse and not being discernable in the DMA analysis and could explain the results obtained by mechanical testing. A secondary relaxation event, not thought to be melting, was observed in the DMA analyses at a temperature between 130 and 180°C. An increase was seen in the temperature at which this event occurred with increased number of thermal cycles.

The observed decrease in both the Loss and Storage Moduli seen in the DMA data for materials with an increasing number of thermal cycles was contradictory to what would be expected based on the experimentally measured mechanical testing data presented in this paper. It is currently not understood by the authors why this contrast between data from mechanical testing and DMA analysis exists. Additional work is needed to understand the structural changes occurring in the matrix of these materials after thermal cycling and to determine the effects of thermal cycling on the magnetic properties of these materials.

Although fracture toughness was not directly studied in this work, comparative toughness values were estimated from the area beneath the stress/strain curves. It is therefore reasonable to expect that a critical powder volume fraction exists for fracture toughness along with other physical and magnetic properties. Therefore, an optimization must be performed of all properties with respect to powder volume fraction to produce a magnet with both maximum mechanical strength and magnetism.

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